Anomalous Surface Relaxations of Branched-Polymer Melts

Shih-fan Wang,[1] Sewoo Yang,[1] Jaesik Lee,[1] Bulent Akgun,[2,3,4] David T. Wu,[5] and Mark D. Foster[1]
[1]*Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, USA*
[2]*NIST Center for Neutron Research, National Institutes of Standards and Technology, Gaithersburg, Maryland 20899, USA*
[3]*Department of Materials Science and Engineering, University of Maryland, College Park, Maryland 20742, USA*
[4]*Department of Chemistry, Bogazici University, Bebek, Istanbul 34342, Turkey*
[5]*Chemical Engineering and Chemistry Departments, Colorado School of Mines, Golden, Colorado 80401, USA*
(Received 10 October 2012; published 8 August 2013)

The dynamics of thermally stimulated surface fluctuations of 100 nm thick films of long-branched polymers are measured for the first time. In contrast to comparable films of linear or cyclic chains that show no change in viscosity upon confinement, films of 6-pom, 6-star, and 6-end end-branched stars show viscosities, inferred from x-ray photon correlation spectroscopy, as much as 100 times higher than in the bulk. This difference varies in magnitude with chain architecture. Branching has a profound effect on confinement, even for these unentangled chains.

DOI: 10.1103/PhysRevLett.111.068303 PACS numbers: 82.35.Lr, 64.70.pj, 82.35.Gh, 68.03.Kn

Surface fluctuations of complex liquids and soft matter are important for problems ranging from avalanches of granular material [1] to radial growth of clusters [2] to adhesion [3] of polymer films. The surface fluctuations of a polymer film are inextricably linked with the mobility of the film surface, a topic that has attracted a great deal of attention [4–6]. Polymers are preferred materials for studies of the changes in dynamical properties under confinement for polymers, colloids, and small molecules due to the ease with which the properties of polymeric materials may be varied using facile synthetic techniques. It is widely thought that polymer films have a surface layer of mobility higher than that of the bulk [4,5,7–10]. It has been suggested that this mobility can be propagated deeper into the film by some mechanism involving cooperatively rearranging regions [8,9]. Roth *et al.* [8] contend there are two mechanisms for the propagation of mobility into the film, one that is independent of connectivity and one that is dependent on connectivity. Thin films of branched polymers are ideal to test these ideas because chain connectivity can be varied synthetically in precise and subtle ways.

The control of branched-polymer topology is a proven means of tailoring bulk melt rheology over a wide range of behaviors [11–19]. Melts of long-branched polymers can have bulk viscosities much lower than those of melts of linear chains with the same average molecular weight when the arm molecular weight is less than the entanglement molecular weight [20]. Studies of entangled branched polymers find that the introduction of long-chain branching dramatically alters the bulk chain relaxation for star [12–14], comb [15,16], H-shaped [17], and dendritically branched [18,19] chains. In contrast, very little is known of the surface relaxation of melts of long-chain branched polymers, though recent work addresses the impact of star-branching on the T_g [21] and physical aging of polystyrene (PS) films [22]. Since the wetting, adhesion, and tribology of polymer surfaces are impacted by thermally stimulated surface fluctuations of the melt, and by surface roughness after vitrification, it is important to understand the dependence of surface fluctuations on chain architecture.

In pioneering work, Kim *et al.* [23] measured surface height fluctuations of linear polystyrene (PS) melts with x-ray photon correlation spectroscopy (XPCS). The surface relaxations behaved as expected from a hydrodynamic continuum theory (HCT) [24,25] that assumes the film behaves as a single layer of uniform viscosity. They further showed [23] that for 123×10^3 g/mol linear PS melt films of different thicknesses greater than four times the chains' radius of gyration, R_g, the surface height relaxation data collapsed onto a single universal curve, as expected from the HCT using bulk viscosity. Thus film viscosities inferred from the XPCS data were found to agree with values from bulk rheometry. Surface height relaxations for films of thickness less than $4R_g$ were slower than anticipated by the HCT and a finite elastic modulus was added to the model to fit the XPCS data [26]. Agreement between bulk viscosities and film viscosities inferred using the HCT has also been reported for sufficiently thick films of small cyclic chains [27].

In this Letter, we report the effects of branched chain architecture on surface height fluctuations using well-defined chains unentangled in the bulk. These first XPCS measurements from long-branched chain melts show a single exponential relaxation time behavior and dependence of relaxation time on wave vector in agreement with the HCT. However, film viscosities substantially larger than the bulk viscosities must be used to fit the XPCS data, suggesting that confinement strongly alters relaxation for the branched chains. It further appears that the fragilities of the branched chains are decreased in these 100-nm-thick films relative to the bulk values, while the fragility of the linear chain is unchanged. Among the

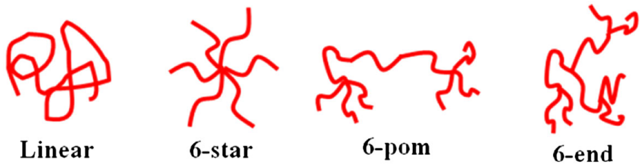

FIG. 1 (color online). Schematics and abbreviated names of the architectures of the linear, six arm star-branched, six arm pom-pom, and six arm, end-branched star polystyrenes.

branched chains the fragility change with confinement is distinct for each architecture.

To incisively study the role of branching it is essential to control other variables, such as chain chemistry, molecular weight, and molecular weight distribution. A novel collection of branched polystyrenes with narrow molecular weight distribution and number average molecular weights of nominally 36×10^3 g/mol synthesized by anionic polymerization and extensively characterized [28] addresses this key need. The architectures of the polystyrenes, which vary in degree of branching from linear to 6-end, end-branched star, are shown in Fig. 1 and their molecular characterization data presented in Table I. The storage and loss moduli (G' and G'') of the polymers measured at angular frequencies (ω) from 0.1 to 100 rad/s in shear oscillatory mode [29] show that all of the molecules are unentangled in the bulk.

Approximately 100 nm thick films were prepared by spin casting toluene solutions onto clean silicon wafers from which the native oxide had been etched. To remove solvent and relax casting-induced stress, films were annealed for 12 h at 150 °C. Film thicknesses were measured by x-ray reflectivity before and after XPCS measurement at each temperature. The XPCS experiments were performed at beam line 8-IDI [23] at the Advanced Photon Source using a $20 \times 20\ \mu\text{m}^2$ monochromatic x-ray beam ($E = 7.35$ keV), with coherence lengths of 7 and 140 μm in the horizontal and vertical directions, respectively. Off-specular scattering patterns were collected for values of in-plane wave vector, $q_\parallel$, up to 10^{-2} nm^{-1}. An incidence angle of 0.14°, which is below the critical angle of PS (0.16°), ensured that x-ray penetration was restricted to 9 nm so that scattering from the polymer-vacuum interface dominated the speckle pattern. Temperatures above the bulk glass transition temperatures, $T_{g,\text{bulk}}$, of the chains, between 90 °C and 150 °C, were probed for each sample.

The normalized intensity-intensity time autocorrelation function, g_2, characterizing the surface fluctuations is given by

$$g_2(q_\parallel, t) = \frac{\langle I(q_\parallel, t')I(q_\parallel, t' + t)\rangle}{\langle I(q_\parallel, t')\rangle^2}, \tag{1}$$

where $I(q_\parallel, t')$ is the scattering intensity at $q_\parallel$ at time t', the angular brackets refer to ensemble averages over time t', and t is the delay time. A single exponential shape, $g_2(t) = 1 + \beta e^{-(2t/\tau)}$, with contrast β and relaxation time $\tau = \tau(q_\parallel)$ fits every correlation function well. All data sets were checked to exclude later frames in which radiation beam damage could have influenced the correlation function.

The HCT [24,25] finds τ to depend on the uniform film viscosity, η, film surface tension, γ, film thickness, h, and $q_\parallel$. For the case of a nonslip boundary condition at the substrate, for highly viscous polymer liquids a normalized surface relaxation time, τ/h, varies with dimensionless wave vector $q_\parallel h$ as

$$\frac{\tau(q_\parallel)}{h} = \frac{2\eta[\cosh^2(q_\parallel h) + (q_\parallel h)^2]}{\gamma q_\parallel h[\cosh(q_\parallel h)\sinh(q_\parallel h) - q_\parallel h]}. \tag{2}$$

If the HCT is valid, the film viscosity, η_{XPCS}, may be inferred from data of τ/h vs. $q_\parallel h$ by finding the value of η/γ to fit Eq. (2), if γ is known. It is sufficient to estimate the value of γ for the branched molecules with that for the linear analog ($\gamma = 40.7 - 0.0072(t - 20)$ with γ in dyn/cm and t in °C for $M_n = 44 \times 10^3$ g/mol PS [30]) since the trends to be discussed are evident on a logarithmic scale. While the surface tensions of the branched chains are distinct from those of the linear, for these molecular weights the differences are less than five percent [31].

The chain architecture (connectivity) has an important impact on the bulk melt rheology, even for molecules with molecular weights below the critical molecular weight for entanglement (38×10^3 g/mol for PS [20]). Note that values of zero shear viscosity derived from bulk rheology measurements shown in Fig. 2 differ due to architecture even after differences in $T_{g,\text{bulk}}$ have been accounted for by plotting vs $T - T_{g,\text{bulk}}$. The viscosities of the branched

TABLE I. Molecular characterization of polystyrenes and their arm precursors.

Polymer	$M_n{}^{a}$ (g/mol)	$M_w{}^{a}$ (g/mol)	$M_w/M_n{}^{a}$	Arm w/o BD	Arm w BD	Precursor	f^{b}	$[\eta]^{c}$ (cm^3/g)	g^{d}	T_g
Linear	36 600	37 000	1.01	-	-	-	2	20.2	-	104
6-star	36 300	37 800	1.04	6100	6200	-	6	10.2	0.51	91
6-pom	40 500	41 700	1.03	3500	3800	18 500	5.8	17.5	0.87	94
6-end	35 800	36 500	1.02	2900	3000	18 100	5.9	12.8	0.64	91

[a] By SEC with light scattering (± 5%).
[b] Arm functionality calculated using $f = (M_{n,\text{branched}} - M_{n,\text{precursor}})/M_{n,\text{arm}}$ (± 5%).
[c] In toluene at 35 °C(±0.5).
[d] Branching factor, $g = [\eta]_{\text{branch}}/[\eta]_{\text{linear}}(\pm 0.04)$ using value of $[\eta]_{\text{linear}}$ in the Table.

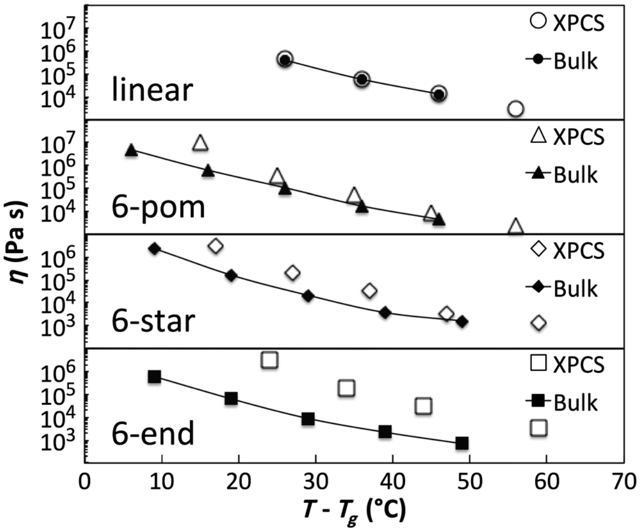

FIG. 2. Comparison of viscosities obtained from XPCS data (open symbols) with viscosities from bulk rheology (filled symbols) as a function of $T - T_{g,\mathrm{bulk}}$ for branched architectures as marked.

chains are all lower than those of the linear analog [29], with the difference being as large as an order of magnitude.

More important for this Letter, however, is that the chain connectivity proves to be important for the surface fluctuation behavior as well, but in a way different than seen for bulk viscosity. The values of τ found for the linear PS chains at 130 °C are in good agreement with the data of Kim *et al.* [23] and the values of η_{XPCS} agree closely with values from conventional rheometry [29] (Fig. 2). The shapes of the time correlation functions for the melt films of branched chains [29] are well fit by a single exponential decay. Also, the variations of τ with $q_{\|}$ for these films are suitably described by the form expected from the HCT [29]. However, when values of η_{XPCS} are derived from the data for the branched chain films, those viscosities are higher than the values derived from bulk rheometry, η_{bulk}, as shown in Fig. 2. This discrepancy is largest closest to $T_{g,\mathrm{bulk}}$ and varies in magnitude with the chain branching. The existence of this discrepancy, its dependence on the branched chain architecture, and its growth in magnitude as $T_{g,\mathrm{bulk}}$ is approached are central observations of this work.

The differences between η_{XPCS} and η_{bulk} are greatest for the most highly branched architecture, 6-end. Those differences are 2 orders of magnitude at the lower temperatures measured. Since the HCT assumes the viscosity is uniform through the film, this suggests that the chain mobility through the film could be as much as 100 times slower than that in the bulk. This is remarkable. For the 6-star sample the effect is less dramatic; in that case the discrepancy is about a factor of 10 at the lowest temperature. Strikingly, the magnitude of the discrepancy between η_{XPCS} and η_{bulk} is distinct for each architecture. We underscore that these large differences are not simply the result of the estimation of γ.

One may attempt, alternatively, to understand the surface relaxation times by modeling the films as containing two layers of quite different viscosity [32]. If the viscosity of a bottom layer next to the substrate is equal to η_{bulk}, the viscosity of the upper layer, η_{surface}, must exceed η_{bulk} by an increasingly larger factor as this high viscosity layer becomes thinner. Using the 6-end sample at 130 °C as an example, if a 70 nm layer adjacent to air has a viscosity higher than the bulk value, η_{surface} must be 10^8 Pa s, which is 4 orders of magnitude larger than the bulk value ($\eta_{\mathrm{bulk}} = 10^4$ Pa s) assumed for the bottom 30 nm of the film. If the thickness of the high viscosity layer is decreased to 10 nm it is impossible to simulate the observed relaxation times, no matter how large η_{surface} is assumed to be. If a more viscous layer is assumed to be next to the substrate, even if we allow the viscosity of that bottom layer to become infinite, its thickness would have to be ca. 70 nm to describe the data. We find it highly improbable that the proper explanation of the unexpectedly slow surface relaxations of the branched chain melts lies in a model with a near surface layer or near substrate layer of such extremely high viscosity.

A growing body of literature suggests that, in fact, there is a thin layer of *reduced* viscosity next to the air on films of linear PS chains [4,5,7–10]. The apparent contrast between those findings and the findings of this work with branched chains is provocative. However, based on the success of the HCT in describing the surface fluctuations of films of linear chains [23], one should not expect XPCS measurements of films of thickness 100 nm to be sensitive to the presence of any extremely thin layer (e.g., <10 nm) of different viscosity at the surface, whether that viscosity be much above the bulk viscosity or much below. If the surface fluctuations depend on flow in the entire film, the entire film thickness would need to be on the order of 10 nm for the XPCS relaxation times to be sensitive to a highly mobile surface layer of the sort proposed by Tsui *et al.* [5] or Ediger and co-workers [7]. So the fact that the analysis with the HCT leads to overall viscosities for the 100 nm thick films of branched chains above those of the bulk does not by itself contradict the possibility of an ultrathin highly mobile layer residing at the surface.

We wish, further, to underscore that while comparison of η_{XPCS} and η_{bulk} provides a convenient means of presenting the anomalous behavior of the branched chain melt surfaces, it is not essential to accept the calculation of the film viscosities with the HCT to appreciate that the branched chain films behave differently than do the linear chain films. Even if one compares simply the temperature dependences of τ/h with those of the bulk viscosities, one can make the observation that those temperature dependences are all distinct for the bulk viscosities, while for the surface relaxation times the temperature dependences for the linear and two branched chain architectures collapse on one another. Also, while on a temperature scale normalized for $T_{g,\mathrm{bulk}}$ the bulk chain dynamics are fastest for the 6-end chain, the surface fluctuations are slowest for that chain. These features may be seen in Fig. 3, which takes the form of the Angell plot [33], in which $T_{g,\mathrm{bulk}}$ is assumed to coincide with a viscosity of 10^{12} Pa s. We have again used η_{XPCS} for plotting, but recognize that since τ/h is proportional to η_{XPCS} (if γ variation with architecture is ignored) relationships among the τ/h values are equally well represented. The Angell plot provides a convenient comparison with literature claims about changes in mobility and fragility under confinement.

If at least relative fragilities can be inferred from the Angell plot, we find that the fragilities of the bulk branched chain melts are all higher than those of the corresponding films, while the fragility of the linear chain melt is unchanged in a film of this thickness. Simulations by Riggleman and co-workers [34] have suggested that the fragility of a polymer liquid film is lower than that of the bulk. Those authors have further argued that polymer film confinement effects should vary with chain molecular structure. In this we find agreement with our results. However, they also reported that mobilities of short linear chains were higher in the film than in the bulk. Perhaps this discrepancy can be explained by noting they studied films with thicknesses (only 9 monomer diameters) much smaller than our film thicknesses and on the order of the thicknesses suggested by Tsui *et al.* [5] and Paeng and Ediger [7] for the highly mobile surface layer itself.

Green and co-workers [21,22] contend that for an 8-arm star with arm molecular weight of 10×10^3 g/mol the T_g of a film increases with decreasing h for h less than 60 nm. Furthermore, for this star they report that positron annihilation lifetime spectroscopy measurements suggest that a local T_g in that star branched melt is as much as 8°C higher at the surface than in the film and the local decrease in mobility (increase in local T_g) persists nearly to a depth of 100 nm. Such an enhancement of the T_g for a branched chain would be consistent with the film viscosity being above bulk viscosity, even for a 100 nm thick film. However, they find that 8 arm stars with longer arms show a decrease in film T_g with decreasing h and a dependence of the T_g depression on the arm length and number of arms.

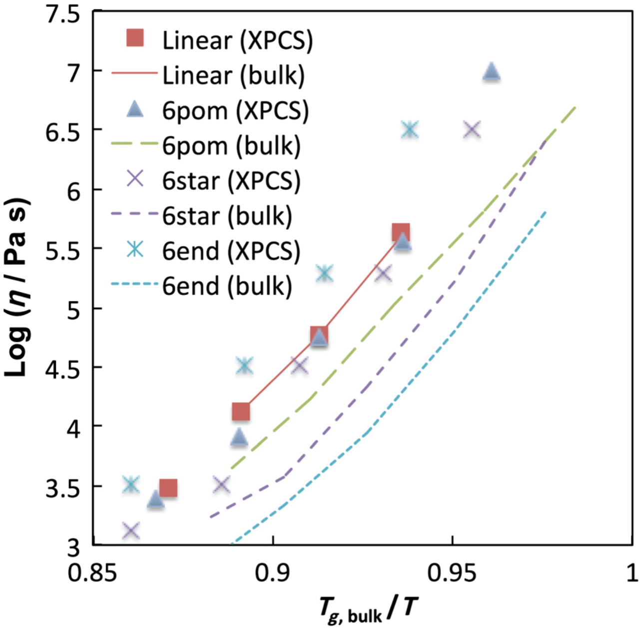

FIG. 3 (color online). Angell plot showing zero shear viscosities of branched chains and linear analog as a function of $T_{g,\mathrm{bulk}}/T$ shown with values of η_{XPCS}.

While the analysis to this point suggests that changes in T_g with chain architecture are important for understanding changes in surface relaxations with architecture, it is possible that there are additional effects as well. When accounting for changes in T_g by considering dimensionless temperature, the data collapse onto a single curve for three architectures. It has been shown separately that such data from cyclic chains of three molecular weights also collapse onto a single curve [27]. The data from the 6-end chain, however, do not follow the collapse seen for the other branched chains. We conjecture that the ease with which the chains move past one another near the surface may depend more profoundly on the way in which they interpenetrate than is the case with the dynamics dictating bulk viscosity. How much a chain penetrates inside the volume pervaded by another chain decreases as the chains become more highly branched. However, the influence of the interpenetration may increase as the chain becomes more highly branched. In the bulk, entanglement for branched chains is much different than that for linear chains. For branched chains to move past one another there must be arm retraction. In the present case of confinement, we do not have entanglement, but there is something qualitatively different about the movement of the chains past one another for the branched chains.

In conclusion, measurements of the surface fluctuations of melt films of unentangled branched polymers reveal strong effects of chain architecture on surface fluctuations, particularly close to $T_{g,\mathrm{bulk}}$. For 100 nm films the surface relaxations are much slower than expected. While differences in surface fluctuation behavior due to chain architecture can be nearly eliminated by accounting for changes in $T_{g,\mathrm{bulk}}$ with architecture, differences in bulk viscosity with architecture are not. This observation, independent of any specific model for the mechanism of surface fluctuation dynamics, suggests that for these branched chains, even for a film as thick as 100 nm, the relaxation mechanism is different than that in the bulk. While accounting for changes in $T_{g,\mathrm{bulk}}$ collapses the data for three of the architectures, this collapse is not achieved when the polymers become sufficiently branched for the phenomenon of chain interpenetration to be more influential. This suggests a profound effect of branching on how confinement affects T_g and the cooperativity (i.e., fragility) characteristic of dynamics at temperatures approaching the glass transition. Further understanding of the alteration of local dynamics and dynamical cooperativity by long-chain branching, even in what is conventionally regarded as a regime of unentangled behavior has implications for a wide variety of applications involving adhesion, wetting, and tribology of thin films.

We thank David Simmons for very helpful discussions, Liang Hong for valuable advice, YangYang Wang for measuring bulk rheology, and to Zhang Jiang and Suresh Narayanan of APS for assistance with XPCS and analysis. This work was supported by NSF Grants No. CBET-0730692 and No. CBET-0731319. The Advanced Photon Source was supported by the U.S. Department of Energy, Office of Basic Science, under Contract No. DE-AC02-06-CH11357.

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